SF 298 MASTER COPY KEEP THIS COPY FOR REPRODUCTION PURPOSES

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE
29 September 1996

3. REPORT TYPE AND DATES COVERED
Final 1 Aug 92 - 31 Jul 95

4. TITLE AND SUBTITLE
GROWTH AND MICROSTRUCTURE OF PROTECTIVE CERAMIC FILMS ON ALUMINUM

5. FUNDING NUMBERS
DAAL03-92-G-0372

6. AUTHOR(S)
Henry W. White

7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES)
UNIVERSITY OF MISSOURI
COLUMBIA, MO 65211

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER
ARO 30134.1-MS-EPS

11. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

12 b. DISTRIBUTION CODE

19961021 158

13. ABSTRACT (Maximum 200 words)

The motivation for this collaborative work with T. Sugama and co-workers at Brookhaven National Laboratory is to develop a low temperature ceramic coating process suitable for aluminum and magnesium. Their method uses sol-precursor solutions with polygermanosiloxane (PGS) or polytitanosiloxane (PTS) additive. Crosslinked networks are formed by pyrolytic reactions near 350°C. The surface microstructure of these films were investigated by Raman spectroscopy, AFM, SEM and EDAX. AFM scans of a 30% TSPI, 20% PTS ceramic film on Al 6061 showed prominent cracks, indicating imperfect match of Al and ceramic film thermal expansion coefficients. Single element scans of the surface reveal highest levels of Al occurring in the cracks, as would be expected because the ceramic film is thinnest at the cracks. However, the ceramic film may not be zero in the cracks, and may afford some level of corrosion protection, if the crack is not too wide. These studies indicate that obtaining crack free films is difficult. Optical spectroscopy showed evidence for Si-O-Ge linkages, and for interfacial oxane bonding with the substrate in the PGS films.

14. SUBJECT TERMS
CERAMIC, COATING, ALUMINUM, MAGNESIUM, LOW TEMPERATURE, POLYGERMANOSILOXANE, POLYTITANOSILOXANE

15. NUMBER IF PAGES
6

16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

DTIC QUALITY INSPECTED 1

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. 239-18
298-102

GROWTH AND MICROSTRUCTURE OF PROTECTIVE CERAMIC FILMS ON ALUMINUM

FINAL TECHNICAL REPORT

BY

HENRY W. WHITE

PRINCIPAL INVESTIGATOR

SEPTEMBER 29, 1996

U.S. ARMY RESEARCH OFFICE

GRANT NO. DAAL03-92-G-0372

UNIVERSITY OF MISSOURI

COLUMBIA, MO 65211

STATEMENT OF THE PROBLEM

The motivation for this work is to develop a low temperature ceramic coating process suitable for aluminum and magnesium. Ceramic coatings offer many advantages, but are not widely used on softer metals. A useful ceramic coating for Al or Mg should have a temperature expansion coefficient similar to that of the substrate metal, and the coating process should not require high temperatures. Many ceramic coatings must be applied or processed above 1000°C. Ceramic films possess the potential for both mechanical and corrosion protection for soft metals. To be useful the film must remain mechanically compact and adhere well to the metal substrate.

Sugama et al.[1,2] have developed ceramic coatings for aluminum for corrosion protection with room temperature application and low temperature processing. The method uses sol-precursor solutions with polygermanosiloxane (PGS) or polytitanosiloxane (PTS) additive. Crosslinked networks are formed by pyrolytic reactions near 350°C.

The goals of the current effort are to investigate the surface microstructure of these films, and to relate the microstructure to composition and other film growth parameters. The techniques employed include Raman spectroscopy, AFM, SEM and EDAX.

SUMMARY OF THE MOST IMPORTANT RESULTS

The sequence for preparing a 30% N-3-[triethoxysily)propyl]-4,5,-dihydroimidazole (TSPI) with 20% polygermanosiloxane (PGS) coating on an aluminum substrate is given below. This coating would be labeled as 30% TSPI, 20% PGS. Aluminum specimens used were nominally 1 cm^2 in area and 1 mm thick.

- washed with methanol, followed by acetone, and then tissue wiped
- etched by an alkaline solution consisting of 0.4wt% NaOH, 2.8 wt% tetrasodium pyrophosphate, 2.8 wt% sodium bicarbonate, and 94.0 wt% water, for 20 min. at 80°C
- washed at 35°C for 5 min.
- baked in a 50°C oven for 30 min.
- dipped in the following solution, with composition indicated, and slowly removed:

TSPI	30 wt%

$Ge(OC_2H_5)_4$	20 wt%
CH_3OH	30 wt%
Water	20 wt%
HCl	15 wt% of combine wt. of TSPI + $Ge(OC_2H_5)_4$

- baked at 150°C for 20 hrs.
- baked at 350°C for 30 min.

Similar coating can be prepared with titanium, in place of germanium, using titanium(IV) ethoxide, $Ti(OC_2H_5)_4$. The performance of PTS films appear to exceed those of PGS. Some specimens with larger areas will be used in future studies to assess possible imperfect wetting due to small surface area.

Sugama et al.[1,2] found several factors were important for forming good films with strong adhesion to the substrate. They were as follows:

- high spreadability of the sol solution
- formation of PGS or PTS at the sintering temperature of 150°C
- enhancement of Si-O-Ge or Si-O-Ti linkages at the pyrolysis temperature of 350°C
- minimal amounts of organic by-products
- formation of an oxane bond from the PGS or PTS to the aluminum oxide.

Figure 1 illustrates the morphology of a 30% TSPI, 20% PTS ceramic film on Al 6061 obtained by AFM. Cracks are evident, indicating imperfect match of Al and ceramic film thermal expansion coefficients. Single element scans of the surface reveal highest levels of Al occurring in the cracks, as would be expected because the ceramic film is thinnest at the cracks. However, the ceramic film may not be zero in the cracks, and may afford some level of corrosion protection, if the crack is not too wide. These studies to date indicate that obtaining crack free films is difficult, requiring careful control of composition and processing.

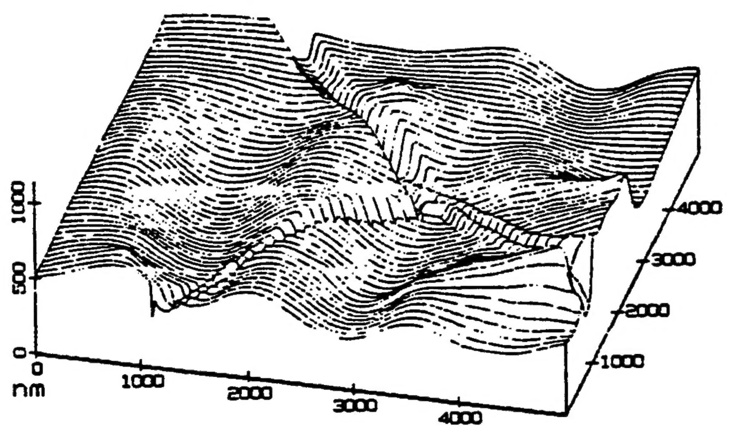

Figure 1. AFM scan of a 30% TSPI, 20% PTS ceramic film on Al 6061.

Optical spectroscopy showed evidence for Si-O-Ge linkages, and for interfacial oxane bonding with the substrate in the PGS films.

LIST OF ALL PUBLICATIONS AND TECHNICAL REPORTS

Journal articles published

"Characterization of Corrosion Protective Films on Steel and Aluminum Alloys," H.W. White, J.E. Chamberlain, J.L. Wragg, F. Mansfeld and T. Sugama, in Nondestructive Characterization of Materials VI, R.E. Green, K.J. Kozaczek and C.O. Ruud, Eds., pp. 757-64, Plenum Press, New York (1994).

"Hydrogen in Polycrystalline Diamond Films Grown by Hot Filament Chemical Vapor Deposition," B. Spytsyn, S. Khasawinah, T. Sung, W.H. Miller, G. Popovici, M.A. Prelas, E.J. Charlson, E.M. Charlson, J.M. Meese, T. Stacy, G. Manning, S. Loyalka, R. Tompson, J.E. Chamberlain and H.W. White, Proc. Third Intern'l Symp. on Diamond Materials, Honolulu, Hawaii, May 16-21, 1993, 93-17, 1032 (1993).

"Raman Scattering and Photoluminescence Characterization of (100) and (111) Oriented Diamond Films Grown in the Same Run by Hot Filament Chemical Vapor Deposition," G. Popovici, S. Khasavinah, T. Sung, M.A. Prelas, B.V. Spitsyn, S. Loyalka, R. Tompson, J. Chamberlain and H.W. White, J. Mater. Res. 9, 2839-44 (1994).

"Ion Beam Surface Modification for Achieving Rectification in Gold-Aluminum Nitride-Silicon Junctions," T. Stacy, B.Y. Liaw, A.H. Khan, G. Zhao, E.M. Charlson, E.J. Charlson, J.M. Meese, M. Prelas, J.L. Wragg, J.E. Chamberlain and H.W White, Proc. of Symp. on Materials Synthesis and Processing Using Ion Beams, Mat. Res. Soc. Symp. Proc. Vol. 316, 355-60 (1994).

"AlN on Diamond Thin Films Grown by Chemical Vapor Deposition Methods," A.H. Khan, J.M. Meese, E.J. Charlson, E.M. Charlson, T. Stacy, S. Krasavinah, T. Sung, G. Popovici, M.A. Prelas, J.E. Chamberlain and H.W. White, SPIE Vol. 2151, Diamond-Film Semiconductors, pp. 44-49 (1994).

Scientific talks presented

"Hydrogen in Polycrystalline Diamond Films Grown by Hot Filament Chemical Vapor Deposition," B. Spytsyn, S. Khasawinah, T. Sung, W.H. Miller, G. Popovici, M.A. Prelas, E.J. Charlson, E.M. Charlson, J.M. Meese, T. Stacy, G. Manning, S. Loyalka, R. Tompson, J.E. Chamberlain and H.W. White, Proc. Third Intern'l Symp. on Diamond Materials, Honolulu, Hawaii, May 16-21 (1993).

"Characterization of Corrosion Protective Films on Steel and Aluminum Alloys," H.W. White, J.E. Chamberlain, J.L. Wragg, F. Mansfeld and T. Sugama, Sixth Inter'l Symp. on Nondestructive Characterization of Materials, Oahu, Hawaii, June 7-11 (1993).

"Smoothing Polycrystalline HFCVD Diamond Thin Films Utilizing Molecular Ion Beams," B.Y. Liaw, T. Stacy, G. Zhao, E.M. Charleson, E.J. Charlson, J.M. Meese, J.E. Chamberlain and H.W. White, Midwest Solid State Conf., Columbia, MO, September 24-25 (1993).

"Micro-Characterization of Cerium-Based Anti-Corrosion Treated Aluminum 6061," Jeffrey E. Chamberlain and Henry W. White, Missouri, Fall Meeting of the Missouri, Illinois and Kansas Microbeam Analysis Society (MIKMAS), Columbia, MO, Nov. 12 (1993).

"Ion Beam Surface Modification for Achieving Rectification in Gold-Aluminum Nitride-Silicon Junctions, T. Stacy, B.Y. Liaw, A.H. Khan, G. Zhao, E.M. Charlson, E.J.

Charlson, J.M. Meese, M. Prelas, J.L. Wragg, J.E. Chamberlain and H.W White, Materials Research Soc. Symp. on Materials Synthesis and Processing Using Ion Beams, Boston, MA, Nov. 29-Dec. 3 (1993).

"Raman Scattering Characterization of (100) and (111) Oriented Diamond Films Grown in the Same Run by Hot Filament Chemical Vapor Deposition," G. Popovici, S. Khasavinah, T. Sung, M.A. Prelas, B.V. Spitsyn, S. Loyalka, R. Tompson, E.J. Charlson, E.M. Charlson, J.M. Meese, J.E. Chamberlain and H.W. White, Symp. on Diamond, SiC and Nitride Wide-Bandgap Semiconductors, Mtg. Material Research Society, San Francisco, CA, 4-8 April (1994).

"Nanocomposite Metal-Diamond Film Growth Using Time-Resolved Emission Spectroscopy," H. W. White and J.E. Chamberlain, American Ceramic Soc. Mtg., Indianapolis, IN, 24-29 April 1994.

"Flash Laser Hardening of Drill Bits," S.L. Thaler, M.S. Hammond, J.E. Chamberlain and H.W. White, Inter'l Conf. on Metallurgical Coatings and Thin Films, San Diego, CA 25-29 April 1994.

REPORT of INVENTIONS

None

LIST OF ALL PARTICIPATING SCIENTIFIC PERSONNEL WITH ANY ADVANCED DEGREES EARNED BY THEM WHILE EMPLOYED ON THE PROJECT

Henry W. White,. Principal Investigator

Jeffrey E. Chamberlain, Ph.D. August 1995

BIBLIGROPHY

1. T. Sugama, N. Carciello, and C. Taylor, Pyrogenic polygermanosiloxane coatings for aluminum substrates, J. Non-Crystal. Solids 134:58 (1991).

2. T. Sugama, L.E. Kukacka, and N.Carciello, Polytitanosiloxane coatings derived from $Ti(OC_2H_5)_4$ modified organosilane precursors, Prog. Org. Coatings, 18:173 (1990).